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Green Polymer Precursors from Biomass-Based Levulinic Acid

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Abstract

Levulinic acid (LA) has been identified as a suitable chemical feedstock that can be isolated from biomass. Its conversion into γ-valerolactone (GVL) via hydrogenation and ringclosure to the lactone has been studied as a versatile route to the manufacture of biodegradable polyesters. For hydrogenation of LA using Ru/C catalyst (the first method), conversion of LA at 100% was observed after 50 min at 90°C in water, with a GVL selectivity of 73%. The product selectivity may be steered by the temperature. At low temperatures 4-HVA is formed selectively, whereas higher temperatures favour the formation of GVL. Meanwhile in the second method, hydrogenation of LA using biphasic water soluble Ru-TPPTS catalysis made in situ in dichloromethane/water biphasic mixtures showed essentially quantitative GVL yields (82%) at 45 bar, 90 °C and 60 min reaction time (1% mol catalyst). As product of the LA hydrogenation, GVL has a very low reactivity for ring-opening due to a very low ring strain. Several studies therefore focused on GVL ring opening into polymerizable compounds but the results so far are unsatisfactory. In this work a novel route has been also investigated using amines for the ring-opening. Because of the basic properties, adding of amine compounds, such as ammonia, aminoethanol, ethylenediamine and piperazine has successfully converted the lactone into compounds containing two functional group viz. alcohol and amide, in essentially quantitative yields. Product design through varying the structure of the amine compound, such as backbone structure and presence of functional groups, appears to be a promising polymer engineering pathway. As such, the novel pathway delivered co-monomers for use in polymer synthesis, to manufacture possible green polymers.

Keywords: Biomass; levulinic acid; hydrogenation; γ-valerolactone; ring-opening; green polymer precursors.

1. Introduction

The ever increasing demand for consumer products such as fuel and polymeric materials and the foreseeable shortage and depletion of crude oil as the major feedstock for the chemical industry has

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prompted several studies into the use of biomass as a renewable source for the extraction or manufacture of platform chemicals. Levulinic acid (LA) is an example of a suitable base-chemical that can be isolated from biomass [1-4]. LA is considered as an important bio-based platform chemical and may serve as a starting material for a wide range of interesting chemicals with a broad application range [1] and a number of interesting derivatives [3,7-9]. Therefore a study on the hydrogenation of LA is part of a potential polymer synthesis route based on levulinic acid.

GVL is typically obtained from LA by stoichiometric reactions or catalytic hydrogenations [9]. Excellent GVL yields (> 98%) have been reported for the hydrogenation of LA using a variety of Ru catalysts (Ru/C [5,10] and Ru/Al_2O_3 [11]). Recently, good results were obtained for catalytic transfer hydrogenation reactions of C6-sugar sources using TFA with formic acid as the hydrogen source using Ru/C as the catalyst [12]. Homogeneous catalysts have also been used for the hydrogenation of LA to GVL using both molecular hydrogen and formic acid as the reductants [13-19]. A drawback of the use of homogeneous catalysts with limited activity is the necessity for catalyst recycles to improve the economic viability of the process. A possible solution is the application of biphasic catalysis, where the catalyst is present in a second phase after reaction and easily separated from the product and recycled [20-22]. A well known approach in homogeneous hydrogenation reactions is the use of aqueous/organic biphasic systems using water soluble ruthenium complexes with sulfonated phosphine ligands like tris(*m*-sulfonatophenyl)phosphine (TPPTS) [23-26]. The aqueous hydrogenation and the biphasic hydrogenation of LA are to the best of our knowledge not reported in the literature.

Furthermore hydrogenation of LA, ring-closure to GVL and subsequent ring-opening [6,27] has been studied as a versatile route for the manufacture of polymers. Unfortunately, the lactone has a very low reactivity due to a very low ring strain [28-30] and direct polymerization resulted in relatively low molecular weight products [31-33]. Nevertheless, several studies have been focused on GVL ring-opening into polymerizable compounds. Brauman *et al.* reported ring-opening of GVL into γ-phenylvaleric acid at 60 ^{o}C for 2 h [34]. Node *et al.* have reacted GVL via ring-opening into γ-alkylthio or γ-arylthio carboxylic acids using AlH_3 catalyst at 25 °C [35]. Van den Brink *et al.* [36] performed the hydrogenation of GVL into pentanoic acid using a strong acidic heterogeneous catalyst comprising a hydrogenating metal such as Pt and Ni on silica or zeolite at a temperature in the range of 100 – 350 °C and pressures until 150 bar. Lange *et al.* reported the esterification and a dehydration of GVL into methyl pentenoate under catalytic distillation at 200 °C [8].

Reaction conditions in these conversions are severe, the product mixtures are complex and the products obtained lack synthetic versatility. Therefore, other chemistry producing more reactive intermediates from LA directly or indirectly by the ring-opening of GVL is desired to develop a new versatile route to produce polymers with high molecular weights. Nelson *et al.* reported that bond cleavage on β-butyrolactone depends on the nucleophilicity of the reagent [37]. Addition of nucleophilic compounds to β-lactone leads to bond cleavage at the γ-carbon-oxygen and at the carbonyl carbon-oxygen, respectively. Furthermore Burba *et al.* have synthesized an amino-amide containing a free hydroxyl-group via addition of di-amine compounds to caprolactone [38].

The reports above suggest that because of their nucleophilicity, amino compounds should be able to open GVL into γ-hydroxy(amino)amide compounds. If this was true, this ring-opening reaction could deliver some promising green precursors through selecting the structure of the amino compound.

In this paper the feasibility of an aqueous hydrogenation using Ru/C catalyst, and a biphasic hydrogenation of LA to GVL in a biphasic water/organic solvent system using the water soluble $RuCl_3$/TPPTS catalyst will be reported. Furthermore the ring-opening of GVL through adding amino compounds such as ammonia, aminoethanol, ethylenediamine and piperazine, has been also reported for synthesizing bioprecursors of polymers. General purpose of this research is to study a novel reaction route to bio-precursors synthesis of polymers through hydrogenating LA followed by ring-opening of GVL.

2. Experiment

2.1. Chemicals (*Chemicals coded as in Scheme 2*)

LA (purity > 98 %), deuterium oxide, D_2O (purity > 99 %) and Ru/C (5 wt% loading on coal char based-carbon active) were purchased from Aldrich. $RuCl_3.3H_2O$ (purity 99%) and Na_3TPPTS were provided by Riedel-de Haen and Strem, respectively. Dichloromethane (DCM) was obtained from Lab Scan (analytical grade, purity 99%). Hydrogen and nitrogen gas were purchased from Hoek-Loos (purity 99.5% v/v). GVL **(1)** (purity ≥ 98%) 1,2-diaminoethane **(4)** (purity ≥ 99%) and 2-aminoethanol **(3)** (purity ≥ 99%) were purchased from Sigma Aldrich. Piperazine **(5)** (purity ≥ 95%) was purchased from Fluka. Ammonia **(2)** (98 vol-% in water) was purchased from Merck. Dimethylsulfoxide, DMSO (purity ≥ 99.7%) was provided by ACROS. Diethyl ether (analytical grade, purity ≥ 99.5%), and n-hexane (analytical grade, purity ≥ 99%) were obtained from Lab Scan. All chemicals were used without further purification.

2.2. Typical procedure of LA hydrogenation with Ru/C in water

The autoclave was charged with water (100 mL). Subsequently, LA (7.37 g, 63.5 mmol) and Ru/C (0.07 g, 1.0 wt% on LA) were added. The stirrer was started (2000 rpm) and the reactor was purged three times with nitrogen. The mixture was heated to 90 °C in about 30 min and subsequently hydrogen was charged to the reactor to a pressure of about 10 bars to saturate the solution with hydrogen. After 10 min, the pressure was increased to 45 bar by hydrogen addition and this point was taken as the start of the reaction. During reaction, hydrogen was admitted to the reactor to keep the pressure at 45 bar. During the reaction, samples were withdrawn from the reaction mixture by a dip tube at pre-determined time intervals. The reaction mixture in the samples was analyzed by NMR to determine the conversion of LA, 4-HVA and GVL yield. After 60 min, the autoclave was cooled to room temperature and vented to atmospheric pressure.

2.3. Typical procedure of LA hydrogenation with Ru-TPPTS in dichloromethane/water biphasic mixtures

The autoclave was charged with Na_3TPPTS (90.4 mg, 0.15 mmol) in DCM (100 mL). Subsequently, LA (1.5 mL, 1.74 g, and 15.0 mmol), $RuCl_3.3H_2O$ (38.1 mg, 0.15 mmol) and water (25 mL) were added. The same procedure with section 2.2. was performed to saturate the solution with hydrogen and to form the active catalyst from the precursors (TPPTS and $RuCl_3.3H_2O$) [23]. After about 10 min, the pressure was increased to 45 bar by hydrogen addition and this point was taken as the start of the reaction. During reaction, hydrogen was admitted to the reactor to keep the pressure at 45 bar. During the reaction, samples were withdrawn from the reaction mixture by a dip tube at pre-determined time intervals. The organic and water phase in the samples were allowed to settle and the organic phase was analyzed by NMR to determine the conversion of LA and the GVL yield. After 60 min, the autoclave was cooled to room temperature and vented to atmospheric pressure.

2.4. Typical procedure of γ-valerolactone ring opening

An amount of 16.25 mmol of amine compound (ammonia, 2-aminoethanol, 1,2-diaminoethane, or piperazine) was mixed with an excess amount of 20.75 mmol of GVL without solvent, and the mixture was stirred at room temperature for 5 h. Separation of the reaction product from the remaining reactants was conducted by adding a mixture of n-hexane and diethyl ether (1:1 v/v) and stirring. The precipitate was decanted and then washed three times using the same solvent mixture. Finally, the precipitate was

dried under vacuum for about 5 h at 70 °C to remove the remaining solvents. The weight of products was determined to calculate the yield of the reactions. The products were characterized by ^{1}H- and ^{13}C-NMR analysis, FTIR and Elemental Analysis.

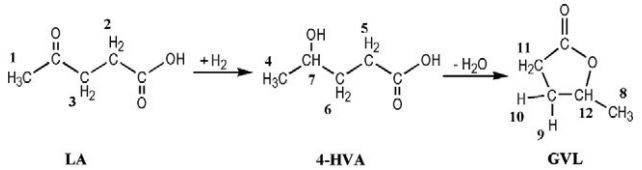
2.5. Analytical procedures

^{1}H- and ^{13}C- NMR spectra were recorded on a Varian AMS 400 MHz spectrometer using D_2O or $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal reference. Multiplicities of proton resonance were designated as single (s), doublet (d), triplet (t), and multiplet (m). FTIR spectra were recorded on a Perkin Elmer FTIR spectrometer (Spectrum 2000 series, resolution 2.0 cm^{-1}, 100 scans). Spectra of solids were recorded using KBr pellets. Vibrational transition frequencies are reported in wave number (cm^{-1}). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br). Elemental analyses were carried out using an Elemental Analyzer (Flash EA 1112, CE Instruments).

3. Results and Discussion

3.1. Hydrogenation of LA with Ru/C in water

For the reaction at given conditions, through a reaction time of 60 min, the concentration of the various components versus batch time was determined by ^{1}H-NMR (Figure 1). The labelling scheme for the hydrogen atoms is given in Scheme 1. The ^{1}H-NMR spectra indicate that the reaction proceeds via the intermediate 4-HVA with characteristic resonances at δ 1.04 ppm (CH_3 group 4), δ 1.61 ppm (CH_2 group 5), δ 2.30 ppm (CH_2 group 6) and δ 3.70 ppm (CH group 7).



Scheme 1. Atom labelling for LA, 4-HVA and GVL

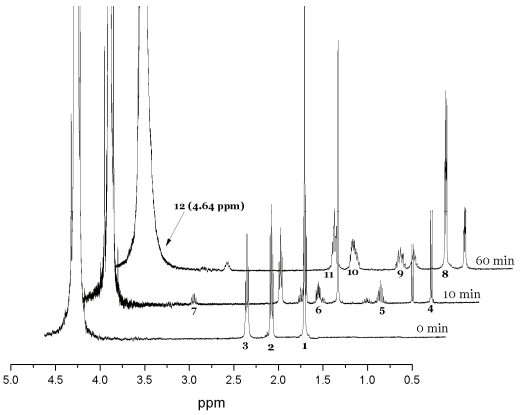


Fig. 1. ^{1}H-NMR spectra (D_2O) at various reaction times for the hydrogenation of LA with Ru/C in water. Peak assignments are given in Scheme 1

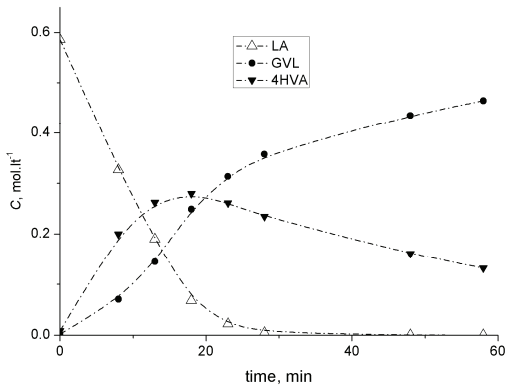


Fig. 2. Reaction profile for the hydrogenation of LA in water using a Ru/C catalyst

The concentration-time profiles were determined experimentally and the results for the methyl base case are provided in Figure 2. The conversion of LA was complete within 50 min reaction time. The highest concentration of 4-HVA was observed at about 18 min. Prolonged reaction times resulted in an increase in the amount of GVL, a clear indication that the reactions proceeded via a consecutive reaction pathway. The relatively high concentrations of 4-HVA during a run is likely caused by the presence of water, which is expected to reduce the rate of the reaction from 4-HVA to GVL due to equilibrium considerations. Temperature variation experiments (50 – 140 °C) showed that at low temperatures 4-HVA is formed selectively, whereas higher temperatures favour the formation of GVL

3.2. Hydrogenation of LA with water soluble Ru-TPPTS in dichloromethane/water biphasic mixtures

The Ru-TPPTS catalyst was made *in situ* by adding the individual components ($RuCl_3.3H_2O$ and sodium-tris(*m*-sulfonatophenyl)phosphine (Na_3TPPTS)) to the reaction mixture instead of an *ex-situ* preparation procedure. The use of a co-solvent or phase transfer agent to transfer the LA from the organic to the water phase is not necessary. Because LA is partly soluble in water (*vide infra*).

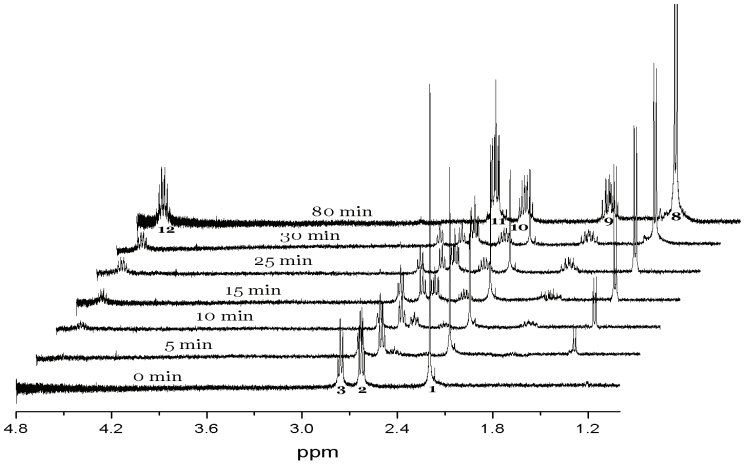


Fig. 3. ^{1}H NMR spectra in $CDCl_3$ of a representative LA hydrogenation run in CM/water using a Ru-TPPTS catalyst. Group labelling is shown in Scheme 1

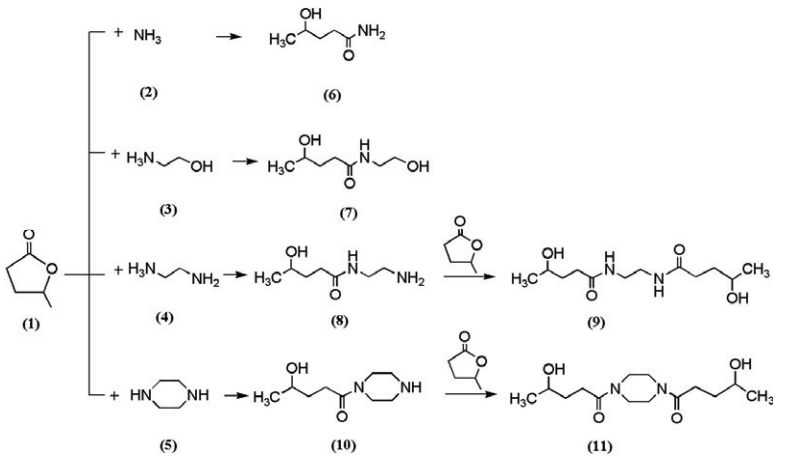
Controlling of the LA conversion during the reactions was performed by taking samples at regular time intervals and subsequent analyses of the organic phase by ^{1}H-NMR. Spectra of H^1-NMR resulted from the typical experiment is given in Figure 3. Clearly visible is the appearance of the methyl group of GVL as a doublet at δ 1.4 ppm and the disappearance of the characteristic methyl group adjacent to the ketone moiety of LA at δ 2.2 ppm.

Referring to Scheme 1, selectivity towards GVL appears to be very high and near quantitative, as confirmed by NMR and GC analyses of the organic phase and HPLC analyses of the aqueous phase. The intermediate 4-hydroxyvalericacid (4-HVA) was not observed, a clear indication that the subsequent lactonisation of 4-HVA to GVL is very fast in the system [33,34]. After 60 min for an experiment, the conversion of LA was 82%. Further investigation in detail was reported in literature [39].

3.3. Ring opening of γ-valerolactone with amine compounds

The ring-opening reactions in this study resulted in the products consisting of γ-hydroxy-amide with methyne, amide and methyl functions (*see* Scheme 2). Characterization of the compounds was performed

by ^{1}H- and ^{13}C-NMR, FTIR and elemental analysis. The representative ^{1}H- and ^{13}C-NMR spectra for product **(9)** as one of the products are shown in Figure 4, which is supported by other data shown in Table 1.



Scheme 2. Synthesis of GVL **(1)**-derived γ-hydroxy-amides through the addition of amino compounds

Table 1. Analytical data for one of products resulted from the ring-opening reaction of **(1)** with **(4)**

Product	Chemical Structure Appearance & Elemental Analysis	^{1}H-Chemical Shift (ppm)	^{13}C-Chemical Shift (ppm)	FTIR (cm^{-1})
(9) 98% (yield)	*N,N'-1,2-ethanediylbis-(4-hydroxy-pentanamide)* $C_{12}H_{24}N_2O_4$,, white powder Anal. Calcd: 55.36% C; 9.29% H; 10.76% N. Found: 55.38% C; 9.33% H; 10.71% N.	(H-1) 1.03 (H-2) 1.58 (H-3) 2.15 (H-4) 3.65 (H-5) 3.17	(C-1) 21.85 (C-2) 32.37 (C-3) 34.16 (C-4) 38.72 (C-5) 67.19 (C-6) 176.89	3276 (free N-H, br) 2907-2964 (H-bonded N-H, m) 1639 (C=O in amide, s) 1555 (stretched C-N & bended N-H, s)

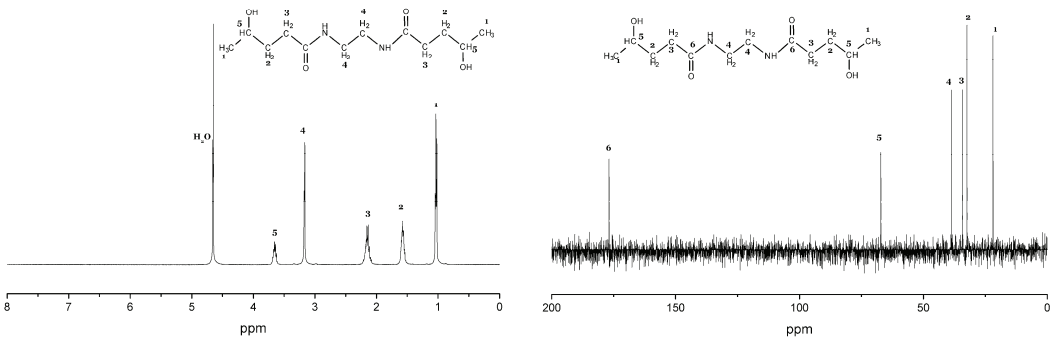


Fig. 4. ^{1}H-NMR and ^{13}C-NMR spectra of product **(9)** in D_2O at 25 °C

The typical functional groups were also obtained from the ring-opening of GVL through adding di-amines such a **(4)**. Figure 5 represents the formation of the products **(8)** and **(9)** during the reaction as

monitored by measuring NMR spectra at regular time intervals. The ^{1}H-NMR spectra can also be used as additional evidence for the sequential formation of the mono- and the di-adduct product during the reaction.

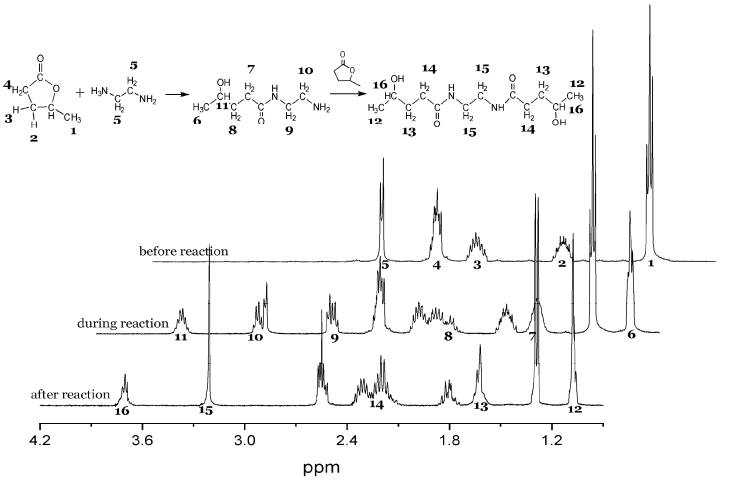


Fig. 5. ^{1}H-NMR spectra for the reaction of **(4)** [8.125 mmol] and **(1)** [41.5 mmol] at 25 °C

The experimental results above suggest that amino compounds because of their nucleophilicity, are able to open γ-valerolactone into γ-hydroxy(amino)amide compounds under mild conditions. The lactone ring opens *via* a nucleophilic addition of the "hard" amine to the lactone carbonyl and results in the formation of an amide and cleavage of the cyclic ester [37]. Detailed study about behaviour of process parameters such as temperature, reactant composition, type of catalyst and solvent, reported in literature [40]. The ring-opening reaction as shown in Scheme 2, is also able to deliver a promising polymer engineering pathway by properly selecting the structure of the amino compound, e.g. by selecting the proper backbone structure or the presence of functional groups. As such, the novel pathway is expected to deliver co-monomers useful in polymer synthesis, and suitable for the manufacture of polymers such as polyurethanes, polyesters and polyethers.

4. Conclusion

Ru/C is an active heterogeneous catalyst for hydrogenation of LA to GVL in water. The catalyst is even active at 50 °C. Presence of water solvent may reduce the rate of the reaction from 4-HVA to GVL, leading to the relatively high concentrations of 4-HVA during a run. Therefore product selectivity may be tuned to 4-HVA or GVL by adjusting the experimental conditions. Temperature variation experiments on the hydrogenation showed that at low temperatures 4-HVA is formed selectively, whereas higher temperatures favour the formation of GVL

Biphasic catalysis in DCM/water using homogeneous Ru-catalysts made in situ from $RuCl_3.3H_2O$ and sodium-tris(*m*-sulfonatophenyl)phosphine (Na_3TPPTS) allows the synthesis of GVL in quantitative yields at mild conditions. This method also offers some advantages such an easily isolation of GVL product.

γ-Valerolactone **(1)** undergoes ring-opening at mild conditions into various γ–hydroxy-amides by reaction with mono- or di-functional aliphatic primary or secondary amines.

Ring-opening of GVL is a promising novel pathway to di-functional compounds as green polymer precursors, which are suitable for polymer synthesis. Product design through varying the structure of the amines, such as backbone structure and presence of secondary functional groups, appears to be a promising polymer engineering pathway. The application of the green polymer precursors for the synthesis of novel polymers will be an interesting further study.

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